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(54) Printing with ink ribbons

(57) A ribbon for impact printers, such as typewriters or word processor printers, is impregnated with an ink which can be cured on the substrate after printing. The ribbon enables the indelible printing of material using variable information printers. The ink may be cured by U.V. light.

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PRINTER RIBBON

The present invention relates to a novel ribbon for ribbon-type impact printers and to an ink therefor.

Ribbon-type impact printers are printers of the type conventionally used in a commercial office in which the imaging system impacts a ribbon against a substrate, usually paper, whereby the ink is applied to the substrate. Such printers may be a typewriter, or a word processor or computer printer. The term "ribbon" is used herein to cover any ink-bearing fabric or sheet used for transferring ink by impact to a substrate, regardless of shape.

Variable information can be printed from impact printers such as used in the commercial office, where the imaging system is a fully-formed character as on a daisy-wheel or a matrix or needle printer used to form characters. In the latter case, software programmes permit the printing of logos or other non-text indicia.

Such printed information has only been satisfactory on paper or similarly absorbent surfaces and where the printing is not subject to wear, because the conventional ribbon inks which form the image dry either by absorption into the substrate or by adhesion insufficient to withstand subsequent mechanical abrading or washing in detergents.

Conventional ribbon inks on woven nylon ribbons typically comprise pigments - usually carbon blacks although coloured pigments may be used - dispersed in a mixture of all or some of animal, vegetable and mineral oils.

For many years there has been a demand for a system which enables the relatively indelible printing of variable information. For example, the

printing of plant labels often requires the application of information which shows some resistance to abrasion and to climatic conditions, such as sunlight or moisture. Usually the number of labels bearing the same information is small and a system capable of applying variable information would be highly desirable. Another example is that for stock control and other purposes it is often desired to print onto clothing labels a number or mark identifying the particular batch or line (e.g. articles having a particular combination of style and colour). The number of garments to be identified by any one number may be relatively small so that a variable information printing system would be appropriate for the task but the applied numbers or marks would have to be sufficiently resistant to abrasion and washing or dry cleaning.

The printing of indelible indicia, such those required for plant or clothes labels, or metal labels, has conventionally been effected using curable inks applied by non-variable printing techniques, for example litho and letterpress printing. In these techniques satisfactory adhesion of the printed image to non-absorbent substrates such as polyolefin, polyester and other plastics materials in film form or woven or non-woven fabric is achieved. Such printing requires the production of printing plates or cylinders which, although suitable for long printing runs, are not suitable where variable information is required on the printed matter where the run-length could be as low as one print if sequential numbering is required.

According to the present invention there is provided a method of impact printing a substrate comprising striking a ribbon impregnated with curable ink against the substrate to form the printed indicia

and subsequently curing the ink which has been transferred to the substrate.

The invention also includes ribbon impregnated with curable ink and the curable ribbon ink itself.

The fixed image formed on the substrate as a result of performing our new method is more resistant to wear (e.g. abrasion, washing, dry cleaning or hostile weather conditions) than the image formed using conventional ribbons. With suitable inks, the fixed image on, say, fabric is able to withstand considerable abrasion, dry-cleaning fluids, other aggressive fluids such as hydraulic fluids, and to meet the British standards, BS 2747, BS 4923 and BS 1006 for domestic washing. Another example of its use is to provide a cured image on impervious materials which may be exposed to a range of climatic conditions such as sunlight and rain. Such impervious materials may be plastics, e.g. plastics film, or metal, e.g. aluminium or other metal labels. However, any type of substrate material may be used, absorbent, non-absorbent or impervious, specific examples being nylon fabric, wood, paper, aluminium and plastics, such as polyester and polyvinyl chloride.

The ribbon which is impregnated with the curable ink may be a conventional fabric ribbon. Fabrics for such ribbons may be cotton, silk or nylon, with nylon being the preferred material. As nylon is essentially non-absorbent, the ink is held between the fine filaments used to make up the weaving threads. The ink is generally absorbed in an amount of from 25 to 30% of the original weight of the nylon. The oil vehicle used for the inks in conventional fabric ribbons is non-drying, that is the oils are essentially free from double bonds which in drying oils promote autoxidation and subsequent

polymerisation. This requirement is necessary as ribbons are exposed to the oxygen of the air for a considerable time when in actual use and the oily ink must remain fluid and capable of transfer to a printable surface. Similarly, the inks used in accordance with this invention although capable of eventual curing, must remain fluid while impregnated in the fabric. It is the capability of curing after transfer to a surface as a printed character or design which is important.

Alternatively, the ribbon which is impregnated with the curable ink may be a film-based ribbon. For some uses film-based ribbons are replacing fabric ribbons, the primary objective being to obtain sharper definition of printed characters or designs, since fabric ribbons tend to reproduce the fabric structure on the character or design. For example, film-based ribbons containing a curable ink, which itself is maintained in a fluid or uncured state until transferred as a character or design in which final state it can be cured, are included in the present invention. The fluid, transferable, ink used in such film ribbons is similar to that used in fabric ribbons, that is they comprise pigments and dyestuffs dispersed in an oil vehicle. In such film ribbons the function of the fabric as a holding medium is replaced by a polymer or resin matrix, throughout which the oily ink is dispersed in small cells or pores. In this invention the fluid ink comprises, as replacement in part or total for the oil vehicle, materials which change their structure from fluid or liquid state to solid state i.e. polymerise on curing. As with fabric ribbons the ink retained in the pores of the resin structure remains fluid during normal storage conditions and is then capable of being cured or fixed by subsequent

irradiation of printed characters or designs.

Other types of film based ribbons are single strike total transfer ribbons which comprise a film substrate, usually polyethylene or polyester, on which is coated a total transfer ink. The ink is usually applied to the film at a final weight of between 2.0 - 6.0 grammes per square metre.

A conventional total transfer ink comprises a mixture of pigments, resins, oils and additives. For the purpose of this invention a typical UV curable ink of the total transfer type would comprise, a pigment which would usually be carbon black although other coloured pigments may be used, a monomer such as tris (2-hydroxyethyl) isocyanurate triacrylate or other reactive acrylates described below and a photoinitiator, for example 2-chlorothioxanthane. A binder resin may also be incorporated.

Additives such as waxes and oils may also be incorporated into the ink to promote transfer from the film and to enhance specific properties of the cured ink such as scuff and abrasion resistance.

The inks of the invention are ribbon inks which are curable after application to the substrate. Curable inks are well known in non-variable information printing systems, for example the use of ultra violet light in selected wave bands is well established in litho and letterpress printing. However, such known curable inks are generally insufficiently fluid (i.e. are too "stiff") to be used as ribbon inks which must have greater fluidity. The differences between, on the one hand, ribbon inks and on the other hand, litho or letterpress inks are of course well known to those skilled in the art and it can be readily determined whether an ink is suitable for use as a ribbon ink.

The inks of the invention may use the same curing

system as the known curable inks and such curing systems will be familiar to the skilled reader. Commonly, curable inks are cured using U.V. light but this is not the only possibility. In some instances, electron beam curing may be used and in some instances the inks may be cured using visible light.

The preferred method of curing the ink which has been transferred to the substrate in the method of the invention is by U.V. curing. There are a number of different types of U.V. lamps which are readily available and all of which can be used to cure the ink in the method of the invention. Suitable U.V. lamps include high pressure mercury (H.P.M.), medium pressure mercury (electrode), medium pressure mercury (electrodeless) and low pressure mercury (L.P.M.) lamps. The two preferred types are the H.P.M. and L.P.M. lamps.

A typical H.P.M. lamp has a U.V. emittance in the range of 320 to 400 nm. Whilst a lamp of this type cures the curable ink very efficiently, it does suffer from the disadvantage that a large amount of infra-red radiation is emitted, giving rise to a build-up of heat which can cause problems with heat-sensitive substrates. Therefore, the most preferred U.V. lamp is a tubular low pressure mercury vapour lamp which emits U.V. radiation in the range of from 300-460 nm, such as that supplied by Phillips under the trade name fluorescent "TL" Lamp Colour 40W/09N which emits U.V. radiation in the range of from 320-390 nm. For optimum output from this lamp the tube wall should be maintained at approximately 43°C. For some applications it may be desirable to include a reflector in the lamp housing which will have the obvious effect of increasing the intensity at the point of cure. A suitable reflector may be a flat plate type or, in some instances when using a

more concentrated irradiation source, to give a more efficient cure is required, an eliptical or focusing (parabolic) reflector may be used. The reflectors are usually made of polished aluminium which gives a high degree of reflectivity, although other suitable metals may be used.

Depending on the power output of the lamp some sort of cooling of the lamp, reflector and the lamp housing may be required which can either be by forced air or circulated water, or even a combination of the two.

The inks of the invention may generally be formulated essentially by the modification of known ink systems with respect to say fluidity, e.g. by addition or further addition of reactive or non-reactive monomers.

The curable inks of the present invention generally comprise one or more prepolymers, which may be solid or liquid, a modifying vehicle such as a reactive or non-reactive monomer, a suitable photoinitiator, and a dispersed pigment with a suitable wetting agent. Other additives such as stabilisers, waxes and silicones may also be present.

The prepolymer resin will generally be used in an amount of from 20 to 60% by weight, optionally including a further prepolymer. Examples of suitable prepolymer resins are epoxyacrylate, urethan acrylate, polyester acrylate, acrylates of epoxidised oils such as soya bean oil, or polyether acrylate. The further prepolymer may be for example a fatty acid modified epoxy acrylate or a second prepolymer chosen from the first group.

The modifying vehicle or diluent is generally used in an amount of from 10 to 40% by weight. Examples of suitable reactive diluents are isobornyl acrylate, tripropylene glycol diacrylate, 1,6 hexane

diol diacrylate and trimethylol propane triacrylate.

The pigment may be any coloured pigment such as carbon black, lithol rubine pigment or phthalocyanine blue pigment.

Extenders such as calcium carbonate may also be incorporated to aid the production of relatively opaque inks. The total amount of pigment plus extender will generally be less than 25% by weight of total ink. Stabilisers such as benzoquinone may be used to increase the shelf life of the uncured inks.

Other additives, such as finely divided waxes and silicones, may be present to enhance specific properties of the cured ink such as scuff and abrasion resistance.

In one preferred example the ink comprises a liquid prepolymer, (e.g. an epoxy acrylate), in a reactive diluent, such as an acrylate monomer, for example isobornyl acrylate, which acts both as liquid vehicle and cross-linker, an initiator, and carbon black or other pigment. The pigment may be dispersed by any usual pigment dispersing system, such as triple-roll milling or ball-milling, for example.

The initiator may comprise a mixture of individual initiator compounds selected to promote satisfactory curing. Typically, the initiator will comprise one or more individual photo-initiators to promote curing under U.V. light. Examples of initiators for use in the curable inks are 2-chloro-thioxanone, 2-chlorothioxanthane, benzophenone, 1-hydroxycyclohexylacetophenone, 2,2-diethoxyaceto-phenone. The quantity and type of the modifying vehicle or diluent will be selected to produce both the required ink viscosity for application of the ink to the ribbon and desirable curing features, and a suitable quantity can be determined without difficulty.

In some cases an inhibitor such as hydroquinone for example, may be added to the ink to prevent premature curing of the ink while still on the ribbon.

The prepared ribbon may be used in an impact printer in the usual way. In general, the ribbon will be put into a cartridge or wound around a spool for use.

After printing by any suitable impact printing method the image on the substrate is cured as discussed above. The reaction time for curing conventionally printed (litho or letterpress printed) inks is in milliseconds. The print rate associated with usual ribbon-type impact printing mechanisms is such that relatively low power ratings are required, for example 400 watts for a line-speed of 1 to 2 metres per minute. This slower rate of curing is an advantage in improving adhesion of ink to substrates.

The present invention will be further described with reference to the following Examples,

Example 1

	% by weight
Epoxy acrylate	20-60
Fatty acid modified epoxy acrylate	15-30
Isobornyl acrylate	30-40
Benzophenone	2-4
Pigment-carbon black	10-20

Preparation Procedure

1. The pigment is dispersed by triple-roll milling in the prepolymer, together with a portion of the modifying vehicle, to prepare Part 1.

2. The photointiator, stabilizer and any other ingredients are dissolved or dispersed in the remainder of the modifying vehicle to prepare Part 2.

3. Part 1 is added to Part 2. The mixture is then impregnated into or applied onto a fabric ribbon.

Example 2

	% by weight
Urethan acrylate	20-60
Polyester acrylate	15-40
Dinnol diacrylate	25-40
2-Chlorothioxanthone	2-5
Pigment-phthalocyanine blue	10-20
Polytetrafluoroethylene powder	1-5

The general procedure of Example 1 was followed to prepare a fabric ribbon impregnated with the above ink.

Example 3

	% by weight
Epoxy acrylate	20-60
Isobornyl acrylate	30-40
Benzophenone	2-5
Michler's ketone	0.5-1
Carbon black	10-20

The general procedure of Example 1 was followed to prepare a fabric ribbon impregnated with the above ink.

Examples 1 to 3 are suitable for imaging onto paper substrates (including cast-coated papers).

Example 4

	% by weight
Epoxy acrylate	25-40
Urethan acrylate	2-10
Hexane diol diacrylate	25-40
Triethylene glycol diacrylate	2-5
2-Chlorothioxanathone	2-4
2,2-Diethoxyacetophenone	2-4
Carbon black	5-20
Polyethylene powder	1-6
Polyethoxylated nonylphenol	0.5-2

The general procedure of Example 1 was followed to prepare a fabric ribbon impregnated with the above ink.

This Example is suitable for imaging onto plastic surface such as PVC and polyethylene. The prepolymers are selected to give maximum adhesion to non-absorbent substrates.

Example 5

	% by weight
Epoxy acrylate	40-60
Polyester acrylate	2-10
Tripropylene glycol diacrylate	10-20
Benzophenone	4-8
n-Methyl diethanolamine	2-5
Lithol rubine (CI Pigment Red 57.2)	5-16
China clay	2-10

The general procedure of Example 1 was followed to prepare a fabric ribbon impregnated with the above ink.

This example is suitable for imaging onto polypropylene and polyester substrates. The introduction of an amine in conjunction with the aromatic ketone substantially increases the rate of cure.

CLAIMS:

1. A method of impact printing a substrate, comprising striking a ribbon impregnated with curable ink against the substrate to form the printed indicia and subsequently curing the ink which has been transferred to the substrate.

2. A method as claimed in claim 1, wherein the ink is U.V., elecron beam or visible light curable.

3. A method as claimed in claim 2 wherein the ink comprises a prepolymer system, pigment and initiator in a modifying vehicle.

4. A method as claimed in claim 3, wherein the prepolymer system comprises an epoxy acrylate and an acrylate monomer, and the modifying vehicle also comprises the acrylate monomer.

5. A method as claimed in any one of the preceding claims, wherein the printing is effected by a typewriter or by a word processor or computer printer.

6. A method as claimed in any one of the preceding claims wherein the ribbon is a fabric or film ribbon.

7. A method as claimed in any one of the preceding claims, wherein the substrate is non-absorbent or impervious.

8. A method as claimed in claim 7, wherein the substrate is plastics film, woven or non-woven

synthetic fabric or metal.

9. A curable ribbon ink which is capable of being cured after printing.

10. An ink as claimed in claim 9 which is as defined in any one of claims 2 to 4.

11. A ribbon impregnated with an ink as defined in any one of claims 9 to 11.

12. A ribbon as claimed in claim 11 which is a fabric or film ribbon.

13. A method of making a printing ribbon, comprising applying ink as defined in any one of claims 9 or 10 to a ribbon.

14. A cartridge for an impact printer containing a ribbon as defined in claim 12 or prepared by a method as defined in claim 13, or a spool having such a ribbon wound therearound.

15. The use of a curable ink as a ribbon ink.

16. An article carrying printing effected by a method as claimed in any one of claims 1 to 8.

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